Twinning tools in PLATON

Detection and Absorption Correction

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**Merohedral Twins**

- The twin element belongs to the holohedry of the lattice, but not to the point group of the crystal.
- The reciprocal lattices of all twin domains superimpose exactly.
- In the triclinic, monoclinic and orthorhombic crystal systems, the merohedral twins can always be described as inversion twins.
Non-merohedral Twins

- Twin operation does not belong to the Laue group or point group of the crystal.
- In practice there are three types of reflections:
  - Reflections belonging to only one lattice.
  - Completely overlapping reflections belonging to both lattices.
  - Partially overlapping reflections belonging to both lattices.
Non-merohedral Twins
Non-merohedral Twins

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[Diagram showing crystallographic axes and unit cell]
Warning signs

• The $R_{\text{int}}$ value for the higher-symmetry Laue group is only slightly higher than for the lower-symmetry Laue group
• The mean value for $|E^2-1|$ is much lower than the expected value of 0.736
• The space group appears to be trigonal or hexagonal
• The apparent systematic absences are not consistent with any known space group
• For all of the most disagreeable reflections $F_o$ is much greater than $F_c$

(Herbst-Irmer & Sheldrick, 1998)
Non-merohedral Twins

• Non-merohedral twins should be detected on the diffractometer.
• Indexing problems can be solved with
  – Phi- and Phi/Chi-Scans
  – Dirax as indexing program
• Intensities can be obtained with EvalCCD
  – Output: SHELX HKLF5 file
Non-merohedral Twins

• If the structure can be solved and refined, non-merohedral twins can be detected with PLATON
  – Input file: *compound.fcf*
  – GUI: TwinRotMat
  – Command line: *platon –T compound.fcf*
# PLATON

A Multpurpose Crystallographic Tool

(C) 1980-2003 A.L. Spek - 10M-Version: 90503

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Xtal Data (CIF ) m025b.clf- Set 1( 11): m025b
Refl Data (SHELXL ) m025b.fcf [ NO-DIRC] :m025b

INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
Cell 7.4014 8.0163 8.2906 89.41 77.54 74.65 P-1

Analysis of Fo/Fc Data for (Non)Merohedral TwInnLng

Criteria: DeltaI/SigmaI GT. 2.5, DeltaTheta 0.10 Deg.

N(refl) = 2104, N(selected) = 149

2-Rotation about [ 1 4 0 ] Flt: 42(68)
(-0.995 0.499 -0.006) (h1) (h2) Alpha () I = 0.78 Deg.
(0.020 0.995 -0.024) * (k1) = (k2) TPA = 0.29
(0.000 0.000 -1.000) (l1) = (l2)

2-Rotation about [ 1 -1 0 ] Flt: 12(18)
(0.081 -0.919 -0.199) (h1) (h2) Alpha () I = 1.23 Deg.
(-1.081 -0.081 0.199) * (k1) = (k2) TPA = 0.28
(0.000 0.000 -1.000) (l1) = (l2)

2-Rotation about [ 0 1 1 ] Flt: 12(22)
(-1.000 0.000 0.000) (h1) (h2) Alpha () I = 0.33 Deg.
(-0.530 0.044 0.956) * (k1) = (k2) TPA = 0.09
(-0.530 1.044 -0.044) (l1) = (l2)

2-Rotation about [ 0 1 0 ] Flt: 12(36)
(-1.000 0.000 0.000) (h1) (h2) Alpha () I = 2.60 Deg.
(-0.596 1.000 0.095) * (k1) = (k2) TPA = 0.22
(0.000 0.000 -1.000) (l1) = (l2)

INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
Cell 7.4046 8.0125 8.2856 89.37 77.49 74.67 P-1

Analysis of Fo/Fo Data for (Non)Merohedral Twinninng

Criteria: DeltaI/SLgmaI GT 5.0, DeltaTheta 0.10 Deg.

N(refl) = 2103, N(selected) = 166

2-Rotation about [ 1 4 0 ] (0 1 0) Flt: 53( 82)
(-0.995 0.499 -0.008) (h1) (h2) Alpha () () = 0.82 Deg.
( 0.021 0.995 -0.025) * (k1) = (k2)
( 0.000 0.000 -1.000) (l1) = (l2)

2-Rotation about [ 0 1 0 ] (-4 12 1) Flt: 20( 52)
(-1.000 0.000 0.000) (h1) (h2) Alpha () () = 2.64 Deg.
(-0.595 1.000 0.084) * (k1) = (k2)
( 0.000 0.000 -1.000) (l1) = (l2)

2-Rotation about [ 1 1 0 ] (9 7 -2) Flt: 15( 35)
( 0.140 0.060 -0.230) (h1) (h2) Alpha () () = 1.11 Deg.
( 1.140 -0.140 -0.230) * (k1) = (k2)
( 0.000 0.000 -1.000) (l1) = (l2)

2-Rotation about [ 1 0 1 ] (-3 8 12) Flt: 12( 24)
( 0.189 -0.300 0.811) (h1) (h2) Alpha () () = 0.52 Deg.
( 0.000 -1.000 0.000) * (k1) = (k2)
( 1.189 -0.300 -0.169) (l1) = (l2)
**TwInRotMat**

**Analysys of F0/Fc Data for (Non)Merohedral TwInLnG**

**Criteria:** DeltaI/Std.gma GT. 2.5, DeltaTheta 0.10 Deg.

N(refl.) = 2109, N(selected) = 206

2-Rotation about [ 1 4 0 1 ] [ 0 1 0 ] Ftt: 74 (99)

(-0.996 0.499 -0.008) (h1) (h2) Alpha () [] = 0.78 Deg.
( 0.018 0.996 -0.024) * (k1) = (k2) TPA = 0.47
( 0.000 0.000 -1.000) (l1) = (l2)

2-Rotation about [ 0 1 0 1 ] [ -4 12 1 ] Ftt: 22 (51)

(-1.000 0.000 0.000) (h1) (h2) Alpha () [] = 2.62 Deg.
(-0.596 1.000 0.094) * (k1) = (k2) TPA = 0.35
( 0.000 0.000 -1.000) (l1) = (l2)

2-Rotation about [ 1 0 1 1 ] [ 12 -3 8 ] Ftt: 16 (27)

( 0.189 -0.301 0.811) (h1) (h2) Alpha () [] = 0.54 Deg.
( 0.000 -1.000 0.000) * (k1) = (k2) TPA = 0.28
( 1.189 -0.301 -0.189) (l1) = (l2)

2-Rotation about [ 1 1 0 1 ] [ 9 7 -2 ] Ftt: 16 (38)

( 0.138 0.862 -0.229) (h1) (h2) Alpha () [] = 1.09 Deg.
( 1.138 -0.138 -0.229) * (k1) = (k2) TPA = 0.36
( 0.000 0.000 -1.000) (l1) = (l2)

**INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)**
Non-merohedral Twins

- TwinRotMat has an option to generate a HKLF5 file based on the twin matrix.
- Warning: The amount of overlapping reflections depends not only on the twin matrix:
  - (Anisotropic) mosaicity
  - Crystal size
  - Detector distance and rotation angle
  - Etc.
- Better: EvalCCD
Example

• Three different crystals of the same compound
• Crystal 1 [BASF 0.0878(19)]:
  • $R_1$ (obs.) 0.0233, $wR_2$ (all) 0.0591, $-0.47/1.38 \text{ e/Å}^3$
  • $R_1$ (obs.) 0.0211, $wR_2$ (all) 0.0534, $-0.38/0.50 \text{ e/Å}^3$
• Crystal 2 [BASF 0.5482(7)]:
  • $R_1$ (obs.) 0.1323, $wR_2$ (all) 0.3361, $-2.29/12.99 \text{ e/Å}^3$
  • $R_1$ (obs.) 0.0282, $wR_2$ (all) 0.0693, $-0.59/0.64 \text{ e/Å}^3$
• Crystal 3 [BASF 0.228(2)]:
  • $R_1$ (obs.) 0.0481, $wR_2$ (all) 0.1340, $-0.62/3.83 \text{ e/Å}^3$
  • $R_1$ (obs.) 0.0261, $wR_2$ (all) 0.0658, $-0.48/0.51 \text{ e/Å}^3$
Pseudo-merohedral Twins

- These are non-merohedral twins, where all reflections seem to overlap because of the limited resolution of the equipment.
- Because cell parameters are temperature dependent, a temperature change can lead to splitting of reflections.
- Pseudo-merohedral twins are optimally suited for TwinRotMat.
Absorption Correction

- With reflections in HKLF4 format, all methods of absorption correction in PLATON are applicable:
  - ABSPsiScan
  - ABSTompa/ABSGauss
  - MULscanABS
  - DELrefABS
  - TWIN/BASF card in `compound.res` is treated properly.
Absorption Correction

- With reflections in HKLF5 format, only analytical absorption corrections are possible (ABST/ABSG).
- Direction cosines of all twin domains must be based on the same orientation matrix (e.g. of the first domain).
- In PLATON the option check direction cosines must be switched off.
Absorption Correction

• The shape of the crystal can be optimized using the program EUHEDRAL based on a HKLF4 file.
• The refined crystal shape can then be applied to a HKLF5 file using PLATON.
EUHEDRAL

- A computer program for the refinement of the crystal shape for an analytical absorption correction
EUHEDRAL

- The difficulty with the analytical absorption correction is the determination of the crystal shape
  - Errors in crystal size measurement
  - Presence of other absorbing material (glass, oil, grease)
  - Unclear face indices
• In many laboratories the crystal shape is refined before the absorption correction is performed
• We want to offer a computer program for this purpose, which
  – makes use of the redundancy of area detector data
  – is as flexible as possible
  – is independent of the diffractometer type
  – is running on many UNIX/LINUX platforms
• EUHEDRAL was developed in close relation to the PLATON package.
• A running version of PLATON is therefore needed. ([http://www.cryst.chem.uu.nl/platon](http://www.cryst.chem.uu.nl/platon))
• The reflection data must contain direction cosines as described for SHELX76 (crystal coordinate system).
EUHEDRAL

- All minimizations in EUHEDRAL are based on a merging R-value $R_2$

$$R_2 = w_1 \cdot R_{int} + w_2 \cdot R_{\psi}$$

$$R_{int} = \frac{\sum[abs(int - intmean)]}{\sum(int)}$$

$$R_{\psi} = \frac{1}{n} \sum\left[\frac{int_{max}}{int_{min}} - 1\right]$$
EUHEDRAL

- The program EUHEDRAL can be run on the command line
- or with a graphical user interface (GUI) based on Tcl/Tk
EUHEDRAL

Info: first select ins file
EUHEDRAL

- In a first step the number of reflections is reduced with the routine filter.
- The suitability of this subset can be judged from different projections.
- Several filter criteria are available: Minimal intensity, minimal theta, minimal redundancy, and angular distribution.
EUHEDRAL
EUHEDRAL

• Situation 1
  – Start with a measured crystal shape (faces are indexed and crystal size determined)
  – Refine volume and distances
  – Fine-tune the description by tilting the faces
EUHEDRAL
EUHEDRAL

- Ex. s2422b (Pt-complex, $\mu = 13.60$ mm$^{-1}$)
- Without correction: $R^2 = 1.069$
- Measured crystal shape+size: $R^2 = 0.592$
- Refined crystal shape+size: $R^2 = 0.497$
EUHEDRAL

- Situation 2
  - Crystal shape known, faces not indexed
  - Refinement of crystal orientation with respect to the reciprocal axes
  - Then refinement of volume, distance and tilt
EUHEDRAL

• Situation 3
  – Nothing known about crystal size and shape
  – Start with a dodecahedron model (EUHEDRAL offers 7 different dodecahedrons)
  – Refinement of volume and distance
  – Refinement of orientation and tilt
EUHEDRAL
EUHEDRAL

R2=0.592  R2=0.497  R2=0.480
EUHEDRAL

• No correction
  – $R_{int}=0.1082$
  – $R1(\text{obs. refl.})=0.0353$
  – Res. dens. −3.05/2.05
  – Ellipticity Pt: 1.99

• EUHEDRAL
  – $R_{int}=0.0553$
  – $R1(\text{obs. refl.})=0.0310$
  – Res. dens. −2.20/1.13
  – Ellipticity Pt: 1.71
EUHEDRAL

- EUHEDRAL
  - 0.101-0.342 transmission
  - $R_{\text{int}}=0.0553$
  - $R1(\text{obs. refl.})=0.0353$
  - Res. dens. –2.20/1.13
  - Ellipticity Pt: 1.71

- DELABS (PLATON)
  - 0.280-0.728 transmission
  - $R_{\text{int}}=0.0504$
  - $R1(\text{obs. refl.})=0.0291$
  - Res. dens. –1.64/1.08
  - Ellipticity Pt: 1.58
EUHEDRAL

- Home page:
  www.crystal.chem.uu.nl/distr/euhedral/
Thanks

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  – A.L. Spek and A.M.M. Schreurs for useful discussions.
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